

### 864. *Alkoxy-radicals. Part II.*<sup>1</sup> *Reaction of the Benzyloxy-radical with Inhibitors: Iodine.*

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Direct reaction between the benzyloxy-radical and iodine appears to be very slow, and iodine functions as an inhibitor owing to capture of solvent radicals, formed by hydrogen abstraction by the benzyloxy-radical from the solvent.

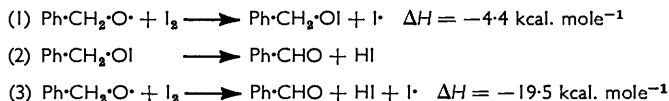
In the most reactive solvent examined, *p*-xylene, the rate of disappearance of iodine was of zero order with respect to iodine and of first order with respect to dibenzyl hyponitrite under the kinetic conditions.

A value of 26.3 kcal. mole<sup>-1</sup> was derived for the activation energy of decomposition of dibenzyl hyponitrite in *p*-xylene; the efficiency of radical production in the same solvent, *ca.* 28%, shows little variation with temperature between 25° and 40°.

RECENT studies on the benzyloxy-radical from benzyl nitrite<sup>2</sup> and dibenzyl hyponitrite have indicated the stability of the carbon skeleton. In particular Gray, Rathbone, and Williams<sup>2</sup> have shown that abstraction of hydrogen and loss of hydrogen (to nitric oxide) by the benzyloxy-radical play an important role in the decomposition of benzyl nitrite. In the present study reactions of the benzyloxy-radical, mainly with iodine but also with other inhibitors, have been examined in order to establish mechanisms of inhibition, the efficiency of radical production in solution, and the apparent activation energy of thermal decomposition, before the work is extended to other substituted dibenzyl hyponitrites.

#### RESULTS

Two direct reactions between the benzyloxy-radical and the iodine molecule may be envisaged:



Reaction (1) is likely to be nearly thermoneutral, whereas hydrogen transfer by reaction (3) appears to be exothermic.<sup>3</sup> Both routes should eventually yield hydrogen iodide which is not detectable in hydrocarbon reaction mixtures under kinetic conditions. In fact the rates of disappearance of iodine from solutions containing dibenzyl hyponitrite are markedly dependent on the solvent, being generally faster the weaker the C-H bond of the solvent. Similar, but less marked, variation of rates with solvent have been observed by Bartlett and Röchardt<sup>4</sup> in the thermal decomposition of *t*-butyl arylperacetates where there is concerted generation of a benzyl and a *t*-butoxy-radical. In this instance there is a two-fold increase in the indicated rate of radical production in changing the solvent from chlorobenzene to toluene. In comparison, dibenzyl hyponitrite shows an approximately seventeen-fold increase in rate on similar change of solvent. In addition, in the kinetic conditions involved in relatively inert solvents such as benzene and chlorobenzene, the amount of iodine that reacts is small and the solutions retain their colour, which is not the case with any of the toluenes except the bromotoluenes. The smaller dependence on solvent in the case of *t*-butyl arylperacetates is probably due to the fact that the substituted benzyl radicals produced scavenge iodine directly in all solvents,

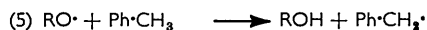
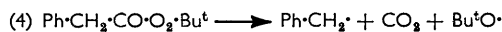
<sup>1</sup> Part I, Ho and de Sousa, *J.*, 1961, 1788.

<sup>2</sup> Gray, Rathbone, and Williams, *J.*, 1960, 3032.

<sup>3</sup> Values calculated from (a) Cottrell, "The Strengths of Chemical Bonds," 2nd edn., Butterworths Scientific Publins., 1958, London, and (b) Gray and Williams, *Trans. Faraday Soc.*, 1959, **55**, 760.

<sup>4</sup> Bartlett and Röchardt, *J. Amer. Chem. Soc.*, 1960, **82**, 1756.

whereas the alkoxy-radical reacts by transfer to solvent where this is efficient, as in the case of toluene, generating a solvent radical which subsequently scavenges iodine:



In toluene and substituted toluenes, dibenzyl hyponitrite gives good yields of bibenzyls, substantiating reaction (5). However, if iodine is added, benzyl iodide was isolated in good yield and was identified as adduct with dimethylaniline, which supports the sequence (5) and (6). Bartlett and Röchardt's work<sup>4</sup> also supports reactions (5) and (6) as the yield of benzyl iodide exceeds one mole per mole of ester, as is required if in this case the iodide is derived from benzyl radicals obtained directly from the initiator as well as from the solvent by reaction (5). In their work, however, no systematic variation in solvent was studied to examine whether the rate (5) of step is determined by bond-energy or other factors. Table 1 gives the rates of disappearance of iodine at 29.7° for thirteen solvents. For solutions in most of the toluene derivatives,  $5 \times 10^{-2}\text{M}$  in dibenzyl hyponitrite and  $10^{-3}\text{M}$  in iodine, the rates are of zero order with respect to iodine provided moisture and oxygen are rigorously excluded, oxygen being found to be as efficient as iodine in trapping benzyl radicals<sup>5</sup> in air-saturated solutions at 30°. For most other solvents the rates measured are slower and not of zero order in iodine (the values given in Table 1 are averages). Fettis, Knox, and Trotman-Dickenson<sup>6</sup> consider that the activation energies for the attack of alkyl radicals on iodine are very small.

TABLE 1.  
Apparent rate constants for the dissociation of dibenzyl hyponitrite (0.05M) in various solvents in presence of iodine (0.001M).

Solvent	$10^5 \times$ Apparent rate constant (sec. <sup>-1</sup> )	Plot of optical density vs. time	Solvent	$10^5 \times$ Apparent rate constant (sec. <sup>-1</sup> )	Plot of optical density vs. time
<i>p</i> -Xylene .....	1.09	100% linear	" Iso-octane " * ...	~0.73 (initial)	Non-linear
Toluene .....	0.95	"	n-Hexane .....	0.70	"
<i>p</i> - <i>t</i> -Butyltoluene	0.76	50% linear	Cyclohexane ...	0.60 (initial)	70% linear
<i>m</i> -Chlorotoluene	0.74	100% linear	<i>t</i> -Butylbenzene	0.24 (initial)	Non-linear
<i>p</i> -Chlorotoluene	0.60	"	Chlorobenzene ...	0.06	"
<i>m</i> -Bromotoluene	0.14	Initially linear	Cumene .....	0.06	"
<i>p</i> -Bromotoluene	0.05	"			

\* 2,2,4-Trimethylpentane.

The kinetic conditions for zero-order dependence on iodine therefore require that the rate of radical production shall be constant, which is only approximately true for the first few per cent of decomposition and if induced decomposition is absent. These conditions will be approached only if the transfer reaction (5) is more efficient than other processes that might lead to the destruction of the benzyloxy-radical, and if the solvent radical formed in step (5) is too stable to induce decomposition by hydrogen abstraction from the parent hyponitrite. Both conditions are more likely to be fulfilled by the toluenes, and this is supported by experiment. The kinetics for the fastest solvent (*p*-xylene) was examined in greater detail, as Bartlett and Röchardt<sup>4</sup> had found that the "efficiency" of radical production from *t*-butyl *p*-methoxyphenylperacetate varied with iodine concentration and temperature. The order of reaction with respect to iodine was determined by a series of runs ranging from  $10^{-4}$  to  $2 \times 10^{-3}\text{M}$ -iodine (Table 2) in presence of  $5 \times 10^{-2}\text{M}$ -dibenzyl hyponitrite; with  $> 5 \times 10^{-4}\text{M}$ -iodine the reaction is of zero order in iodine.

TABLE 2.

[I] ( $10^{-4}$ mole/l.)	1	5	8	10	20
Rate of consumption of I, in optical density units (min. <sup>-1</sup> )	0.016	0.051	0.063	0.065	0.064

In addition, the rate of disappearance of iodine from  $10^{-3}\text{M}$ -solution is a linear function of the concentration of dibenzyl hyponitrite over a range of 0.01—0.1M (Table 3). The rate law for

<sup>5</sup> Gardner and Noyes, *J. Amer. Chem. Soc.*, 1961, **83**, 2409.

<sup>6</sup> Fettis, Knox, and Trotman-Dickenson, *Canad. J. Chem.*, 1960, **38**, 1643.

disappearance of iodine is therefore of zero order with respect to iodine and of first order with respect to hyponitrite, and is given by the equation  $-d[I_2]/dt = k_a[(Ph\cdot CH_2)_2N_2O_4]$ . The apparent rate constants obtained by the iodine method ( $k_a$ ), the true unimolecular rate constant ( $k_d$ ), and the efficiencies of radical production ( $a$ ) at the several temperatures are given in Table 4. The results over the temperature range 25—40° show little variation in the efficiency factor  $a$ . This contrasts with the results for the azoisobutyronitrile-diphenylpicrylhydrazyl system<sup>7</sup> where the efficiency of radical production decreases with increase in temperature.

The Arrhenius plot yields an apparent activation energy of 26.3 kcal./mole<sup>-1</sup>, to be compared with the value of 25 obtained manometrically.

Since the bond-dissociation energies for the benzyl C-H bonds in substituted toluenes do

TABLE 3.

$[(Ph\cdot CH_2)_2N_2O_4]$ ( $10^{-2}M$ ) .....	1.0	2.5	4.0	5.0	6.0	7.5	10.0
Rate [= Change of optical density per min.] .....	0.012	0.024	0.043	0.050	0.064	0.074	0.100
Rate/Concn. ....	1.2	0.96	1.07	1.00	1.06	0.98	1.00

TABLE 4.

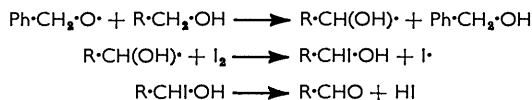
Temp.	25°	27°	29.8°	35°	40°
$k_a$ ( $10^{-4}$ sec. <sup>-1</sup> ) .....	0.0481	0.0641	0.107	0.208	0.420
$k_d$ ( $10^{-4}$ sec. <sup>-1</sup> ) .....	0.178	0.242	0.363	0.723	1.380
$a$ (%) .....	28.0	26.5	29.1	28.8	30.4

not differ greatly<sup>8</sup> and hydrogen abstraction is highly exothermic it is possible that the relative rates of abstraction may reflect polar influences. The rates of disappearance of iodine from solutions in the toluenes examined are all of zero order, except for the bromotoluenes. Apart from the fact that electron-attracting substituents lower the rate there does not appear to be any correlation by means of the Hammett  $\sigma$ - $\rho$  function. This may be due to a variable efficiency of radical production in the several solvents. For the *t*-butoxy-radical, where such a correlation<sup>9</sup> has been observed, the efficiency of radical production from di-*t*-butyl peroxide obtained by means of disappearance of iodine from toluene solutions<sup>4</sup> is 100%; this indicates that in this case no cage reaction reducing the efficiency of radical production occurs. Cumene shows an abnormally low rate of iodine disappearance despite its weak hydrogen bond. A similar effect in the reaction of *t*-butyl arylperacetates with iodine has been observed and explained by Bartlett and Rüdhardt<sup>4</sup> as due either to the instability of cumyl radicals or to regeneration of iodine by other reactions.

With other hydrocarbon solvents the rates of disappearance of iodine are in the order tertiary hydrogen > secondary hydrogen > primary hydrogen, *i.e.*, "iso-octane" > cyclohexane > *n*-hexane > *t*-butylbenzene > chlorobenzene, which is the order for the exothermicities for abstraction of the weakest hydrogen atom by the benzyloxy-radical.

The solvents isopropyl and benzyl alcohol show a somewhat different behaviour. With isopropyl alcohol the optical density corresponding to the iodine peak first increases and then decreases. With benzyl alcohol as solvent this peak remains practically unchanged for 25 minutes and decreases to nearly zero in the next 5 minutes.

The following sequence is suggested:



In keeping with this mechanism silver iodide is precipitated immediately from decolorised benzyl alcohol solutions, and after a few minutes from isopropyl alcohol solutions, in support of the last step of this sequence. Other hydrocarbon solvents, *e.g.*, cyclohexane, do not give silver iodide under the same conditions.

<sup>7</sup> Bawn and Verdin, *Trans. Faraday Soc.*, 1960, **56**, 815.

<sup>8</sup> Ref. 3(a), Chapter 11.

<sup>9</sup> Johnston and Williams, *J.*, 1960, 1446.

Of the three other inhibitors examined, triphenylmethyl, 2,4,6-tri-*t*-butylphenoxy, and diphenylpicrylhydrazyl, only the last was found to be kinetically useful as a scavenger for the study of the decomposition of dibenzyl hyponitrite. In chlorobenzene, for instance, the reaction was found to be of zero order in diphenylpicrylhydrazyl and of first order in hyponitrite. The activation energy obtained for the decomposition of the ester was 25.4 kcal./mole, in agreement with the value of 25 obtained manometrically. Details of the mechanism of the reactions with these inhibitors will be offered later.

#### EXPERIMENTAL

*Materials.*—Benzene, toluene, *p*-xylene, cyclohexane, chlorobenzene, and benzyl alcohol were of B.D.H. grade, purified as previously described,<sup>2</sup> the first four being dried over sodium before final distillation. *n*-Hexane and "iso-octane" of B.D.H. spectroscopic grade were dried by sodium and fractionally distilled in a stream of argon: *n*-hexane had b. p. 69°, and "iso-octane" b. p. 99.5°.

Cumene, b. p. 153°, *t*-butylbenzene, b. p. 53°/10 mm., and *t*-butyltoluene, b. p. 94°/25 mm., were Eastman Kodak reagents, dried over sodium and fractionated in a stream of argon.

Fractional distillation, in argon, of commercial materials (from Messrs. L. Light and Co.) gave *m*-chloro-, b. p. 162°, *p*-chloro-, b. p. 44°/10 mm., f. p. 7.8°, *m*-bromo-, b. p. 183°, and *p*-bromotoluene, b. p. 184°, m. p. 28.5°. Only the middle cuts of the main fractions (2 ft. column, 4 mm. Fenske helices) were used.

Dibenzyl hyponitrite was prepared as previously described.<sup>10</sup>

Iodine of "AnalaR" grade was used.

*Attempted Detection of Hydrogen Iodide.*—A cyclohexane solution (100 ml.), 0.05M in dibenzyl hyponitrite and 0.02M in iodine, was degassed and sealed in a break-seal ampoule. This was kept in a thermostat-bath at 40° for 4 days, the colour of the iodine completely disappearing. The ampoule was then attached to a vacuum-line, and the gases were transferred and absorbed in silver nitrate. No silver iodide was precipitated. Similarly prepared ampoules which were opened under silver nitrate solution did not yield silver iodide.

*Decomposition in Toluene and p-Chlorotoluene.*—Dibenzyl hyponitrite (3 g.) in the respective toluene (100 ml.) was allowed to decompose at 40° in a stream of argon for 4 days. After removal of the solvent the residue was dissolved in ether, shaken with sodium hydrogen sulphite and then water, and dried, and the ether was removed. The residues crystallised from ethanol, giving good yields of bibenzyl, m. p. 52°, and 4,4'-dichlorobibenzyl, m. p. 112°, in the two cases.

*Decomposition in Toluene and p-Xylene in Presence of Iodine.*—Dibenzyl hyponitrite (2 g.) in toluene (50 ml.) was allowed to decompose at 40° in presence of iodine (3 g.) under argon for 4 days. The excess of toluene was removed at 0° in a high vacuum. The residue was dissolved in ether, shaken with ice-cold aqueous sodium thiosulphate and with water, and dried. The ether was then removed, yielding residues of benzyl iodide (odour). These residues, in toluene, gave, on addition of dimethylaniline, the quaternary salt, m. p. and mixed m. p. 157°.

*Kinetic Procedure.*—The rates of reaction were followed spectrophotometrically by means of a Hilger Uvispek instrument fitted with a thermostat-controlled cell-block. Two air-conditioning systems, one of which was adjustable, provided a steady ambient temperature. Water was circulated through the lagged cell-block by means of a Circotherm Mark II apparatus, and the temperature of the cell-block (determined by a thermocouple) was constant within  $\pm 0.05^\circ$ .

The appropriate iodine solution was degassed, by a stream of argon, for 4 hr. in the thermostat-bath from which water was circulated. Solutions of dibenzyl hyponitrite were made and the cells which had been kept in the cell-block were filled immediately with a dropper or syringe without formation of air-pockets.

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<sup>10</sup> Partington and Shah, *J.*, 1932, 2593.